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Unregulated Emissions from Compressed Natural Gas (CNG) Transit Buses Configured with and without Oxidation Catalyst

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Abstract

The unregulated emissions from two in-use heavy-duty transit buses fueled by compressed natural gas (CNG) and equipped with oxidation catalyst (OxiCat) control were evaluated in the present study. We tested emissions from a transit bus powered by a 2001 Cummins Westport C Gas Plus 8.3 L engine (CWest), which meets the California Air Resources Board's (CARB) 2002 optional NO_X standard (2.0 g/bhp-hr). In California, this engine is only certified with an OxiCat, so our study did not include emissions testing without it. We also tested a 2000 New Flyer 40-passenger low-floor bus powered by a Detroit Diesel series 50G (DDC) engine that is currently certified in California without an OxiCat. The original equipment manufacturer (OEM) offers a "low-emission" package for this bus that includes an OxiCat for transit bus applications, thus, this configuration was also tested in this study. Previously, we reported that formaldehyde and other volatile organic emissions detected in the exhaust of the DDCs50 bus equipped with an OxiCat were significantly reduced relative to the same DDCs50 bus without OxiCat. In this paper, we examine other toxic unregulated emissions of significance. The specific mutagenic activity of emission sample extracts was examined using the microsuspension assay. The total mutagenic activity of emissions (activity per mile) from the OxiCat-equipped DDC bus was generally lower than for the DDC bus without the OxiCat. The CWest bus emission samples had mutagenic activity that was comparable to that of the OxiCat-equipped DDC bus. In general, polycyclic aromatic hydrocarbon (PAH) emissions were lower for the OxiCat-equipped buses, with greater reductions observed for the volatile and semi-volatile PAH emissions. Elemental carbon (EC) was detected in the exhaust from the all three bus configurations, and we found that the total carbon (TC) composition of particulate matter (PM) emissions was dominated by organic carbon (OC). The amount of carbon emissions far exceeded the PM-associated inorganic element emissions, which were detected in all exhaust samples, at comparatively small emission rates. In summary, based on these results and those referenced from our group, the use of OxiCat for new CWest engine and as a retrofit option for the DDCs50 engine generally results in the reduction of tailpipe toxic emissions. However, the conclusions of this study do not take into account OxiCat durability, deterioration, lubricant consumption, or vehicle maintenance and these parameters merit further study.

Introduction

Natural gas is a clean alternative fuel and, consequently, CNG-fueled vehicles are generally assumed to emit fewer toxic air contaminants (TAC) than conventional diesel counterparts without air pollution control devices. However, recent studies indicate that CNG-fueled transit buses can emit a wide range of toxic compounds that include mutagens, PAHs, nitro-PAHs, aromatics, aldehydes notably formaldehyde, and metals. The emissions from various types of heavy-duty CNG and diesel transit buses in New York City have been examined using the Central Business District (CBD) test cycle. Several 1999-model year CNG buses with DDC S50G engines were tested and had lower PAH and nitro-PAH emissions than similar uncontrolled diesel-fueled vehicles [1]. Lev-On et al. 2002A reported that the emissions of PAHs and 2-ring nitro-PAHs from a 2000 CNG transit bus were generally lower than those from diesel buses without pollution control devices [2]. However, emissions of nitro-PAHs containing 4 or more fused rings were higher from the CNG bus. A CNG-fueled, lean-burn, turbocharged electronically controlled heavy-duty engine operated over the ECE R49 cycle on an engine dynamometer was reported to have PAH emissions 1 to 3 orders of magnitude lower than a comparable diesel-fueled engine [3]. PAH emissions were detected from CNG-fueled school buses, but not in the emissions from a trap-equipped diesel school bus [4]. PAH emissions have also been detected from CNG-fueled transit buses equipped with a three-way OxiCat at 107 mg/km, while the emissions from transit buses fueled with ECD-1 diesel (10 ppm sulfur) had emission levels that were approximately 121 mg/mi [5]. Our previous study examined PAH emissions from the same bus but without after-treatment. The bus was also tested using several driving cycles including the CBD and SS [6]. High mutagenic activity from this CNG transit bus was observed relative to a diesel bus equipped with both a diesel OxiCat and a catalyzed diesel particle filter (CB-DPF) [6]. Another study has reported mutagenic activity from a LNG-fueled refuse hauler [7].

Using the thermal optical transmittance (TOT) method to determine elemental carbon (EC) and organic carbon (OC) emissions, Lanni et al., found average OC emissions for the CBD cycle ranging from 6 to 14 mg/mi, while EC emissions were below their detection limit [1]. The thermal optical reflectance (TOR) method used for detection of EC and OC by Lev-On et. al.

found that ionic species from two CNG buses for the CBD cycle were emitted at an average rate of 1.0 mg/mi [8]. The OC accounted for approximately 91% of the summed ionic species, EC, and OC emissions. The OC emissions from the CNG buses ranged from 19 to 30 mg/mi while EC emissions were 0.3 mg/mi or less. The testing of tunnel background (TB) samples corresponding to these emissions ranged from 8 to 10 mg OC/mi, while EC levels were below the detection limit.

Recent debate has centered on the possible source of mutagenic, PAH, and nitro-PAH emissions from CNG-fueled vehicles, since unlike diesel fuel, CNG fuel does not contain these compounds or precursors to these compounds. One study has concluded that lubricating oil is a major component of diesel PM [9]. A chase study has been conducted on transit buses including CNG-fueled buses that concluded that the non-refractory part of the emitted PM as measured by aerosol mass spectrometry was dominated by a lubricating oil chemical signature [10]. The obvious source of lubrication oil is the engine, but CNG fuel may contain measurable amounts of compressor oil that comes from the transporting and delivery systems [11]. Transit buses basically operate in densely populated areas where they contribute to urban pollutant exposure [12].

These studies suggests that CNG buses can emit measurable levels of toxic compounds despite total PM emissions that may be considerably lower than conventional diesel vehicles. Therefore, characterizing the toxicity profile and composition of PM from in-use CNG-fueled transit buses and the potential benefit offered by an OxiCat pollution control device for this type of vehicle is important. The California Air Resources Board initiated this study to determine the efficacy of an oxidation catalyst to reduce toxic (especially formaldehyde) and mutagenic emissions from CNG-fueled transit buses. This study is one of the first to systematically evaluate an oxidation catalyst for application on CNG-fueled heavy-duty engines. Previously, we reported that formaldehyde and other volatile organic emissions detected in the exhaust of the DDCs50 bus equipped with an OxiCat were significantly reduced relative to the same DDCs50 bus without OxiCat [13]. Specifically, the objective of this paper is to offer the first detailed report on the effect of a CNG OxiCat on mutagenic and other PM-associated toxic emissions.

Experimental Methods

Vehicles and Test Location

A 2001 Cummins Westport C Gas Plus 8.3 L bus (CWest) was tested, which meets the 2002 CARB optional NO_X standard (2.0 g/bhp-hr). In California, this engine is only certified with an OxiCat, so our study did not include testing without it. This lean-burn, spark-ignited, 6 cylinder, turbocharged engine with a compression ratio of 10:1 and electronic engine management with full control of air/fuel handling and drive-by-wire function has been described in additional detail by Kamel et al. (2002). [14]. We also tested a 2000 New Flyer 40-passenger low-floor bus powered by a DDC S50G engine with and without an OxiCat. The DDCS50G engine is an 8.5L, 4 cylinder, turbocharged engine with closed loop fuel control, electronic spark ignition, and a compression ratio of 10:1. Additional information is readily available on the engine manufacturer's website [15]. The OxiCat is a retrofit package that Detroit Diesel makes available for DDC S50 G engines, but its design and formulation are proprietary. The retrofit installation of the OxiCat was conducted by the engine manufacturer. Emissions testing was conducted at the CARB Heavy-Duty Emissions Testing Laboratory (HDETL) located at the Los Angeles County Metropolitan Transit Authority (LACMTA) Regional Rebuild Center in downtown Los Angeles [13]. Regulated and unregulated emissions were collected simultaneously and some results have been already reported by our group [13].

Fuel and Oil Properties

The CNG fuel used for the test buses was obtained from a refueling station that supplies the LACMTA for normal operations. The CNG fuel is taken directly from the pipeline that provides fuel for the Los Angeles area. Fuel samples were collected prior to bus testing and were analyzed by a commercial laboratory (Quantum Analytical Services Inc., Carson, CA). All fuel samples were determined to meet the State of California specifications for CNG motor vehicle fuel [16]. The lubricating oil was also analyzed by a commercial laboratory (Oil Science Laboratory, Lawndale, CA) prior to vehicle testing. Results for the analysis of the fuel and lubricating oil for each test bus met specifications and are summarized in Tables 1 and 2, respectively.

Table 1. CNG Fuel Sample Analysis Results.

Compound	Fuel Composition (%)		
	DDC w/oOxiCat[a]	DDC wOxiCat[b]	CWest wOxiCat[c]
Methane	94.3	93.8	96.7
Ethane	2.0	1.5	0.7
Ethylene	<0.1	<0.1	<0.1
Propane	0.4	0.4	0.1
Propylene	<0.1	<0.1	<0.1
i-Butane	<0.1	<0.1	<0.1
n-Butane	<0.1	<0.1	<0.1
1-Butene	<0.1	<0.1	<0.1
trans-2-Butene	<0.1	<0.1	<0.1
cis-2-Butene	<0.1	<0.1	<0.1
i-Pentane	<0.1	<0.1	<0.1
n-Pentane	<0.1	<0.1	<0.1
1-Pentene	<0.1	<0.1	<0.1
2,2-Dimethyl Butane	<0.1	<0.1	<0.1
2,3-Dimethyl Butane	<0.1	<0.1	<0.1
2-Methyl Pentane	<0.1	<0.1	<0.1
3-Methyl Pentane	<0.1	<0.1	<0.1
n-Hexane	<0.1	<0.1	<0.1
1-Hexene	<0.1	<0.1	<0.1
C_6+	<0.1	<0.1	<0.1
CO_2	1.3	1.3	0.1
CO	<0.1	<0.1	<0.1
O_2	0.05	<0.1	<0.1
N_2	1.9	3.0	2.4
H_2	<0.1	<0.1	<0.1
H_2S	<0.1	<0.1	<0.1

[a] Fuel sample collected on 5/28/02
[b] Fuel sample collected on 5/13/02
[c] Fuel sample collected on 4/23/02

Table 2. Results of Lubricating Oil Analysis.

Component	Units	Test Vehicle		
		DDC w/oOxiCat[a]	DDC wOxiCat[b]	CWest wOxiCat[c]
Iron	ppm	5	12	14
Zinc	ppm	1041	441	440
Phosphorus	ppm	800	345	338
Calcium	ppm	1013	1090	1094
Copper	ppm	73	5	5
Lead	ppm	<1	3	3
Boron	ppm	14	23	22
Silicon	ppm	2	4	4
Sodium	ppm	<1	5	5
Viscosity	SUS	485	440	439
Soot/PM[d]	n/a	Normal	Normal	Normal
Sulfur	% wt	0.307	0.228	0.227
Chlorine	ppm	25	12	22
Engine wear metals	n/a	Normal	Normal	Normal

[a] Fuel sample collected on 5/31/02.

[b] Fuel sample collected on 5/17/02.

[3] Fuel sample collected on 5/3/02.

[d] Proprietary qualifier denotes a normal, abnormal, or severe content of solid soot particles found in an oil sample. This parameter is determined based on oil "blackness".

Dynamometer Testing and Sample Collection

Chassis dynamometer testing and test vehicle characteristics have been previously described [13]. The CBD test cycle and a steady state (SS) 55 mph cruise condition were used in the present study. Test sequences were composed of multiple individual cycles run consecutively to ensure collection of sufficient sample for subsequent chemical analyses. The SS test cycle sequences were approximately 30 min long to coincide with the approximate duration of three consecutive CBD cycles.

Emission sample and tunnel background collection followed a strict and consistent protocol that included a test vehicle conditioning procedure. Prior to sampling each day, the constant volume sampling (CVS) dilution tunnel was allowed to run for approximately 60 min. Then, the bus was run at idle for 15 min. Over the next 20 min, the bus was operated at 55 mph. For the CBD tests, four cycles were run consecutively. The first cycle was used for conditioning and sample collection was executed over the second through fourth cycles. An identical sequence was followed for the SS test cycle. The filters used for collecting PAH and bioassay samples were standard 70 mm Teflon-coated glass fiber filters (T60A20, Pall-Gelman, Ann Arbor, MI). PAH

samples were collected from a secondary dilution tunnel using two filters in series, followed by polyurethane foam (PUF) and XAD-4. Where applicable, the protocols outlined in the Code of Federal Regulations (CFR) for PM sampling were used. PAH samples were collected at a nominal flow rate of approximately 3.5 standard cubic feet per minute (scfm). Bioassay samples were obtained from the primary CVS dilution tunnel at a nominal flow rate of 3 cubic feet per minute at ambient temperature using a probe co-located with other probes used for collection of other emission samples. The bioassay sampling train consisted of two filters, in series, followed by PUF and XAD-4 [6]. Filters were exchanged after sample collection over three cycles (one test sequence) and adsorbent cartridges were exchanged after six cycles (two test sequences).

Samples for EC/OC and inorganic element analyses were collected on Whatman type 40, 47 mm pre-baked quartz fiber filters, respectively, at a nominal flow rate of 28 Lpm. We chose conventional filter material as suggested by the analyzing laboratory. Samples were drawn directly from the primary dilution CVS tunnel using a previously described custom-made dual sampler co-located along with other sampling probes, including the secondary dilution tunnel intake used for the collection of total PM criteria emissions [17]. Inorganic element samples were analyzed by X-ray fluorescence (Desert Research Institute, Reno, NV) using US EPA methodology [18].

EC and OC contents were determined based on the IMPROVE Thermal/Optical Analysis Method (South Coast Air Quality Management District, Diamond Bar, CA) [19]. The method is designed to quantify organic and elemental carbon from deposits of carbon-containing material on filters and the analysis is based on the preferential oxidation of organic and elemental carbon compounds at different temperatures. Expert discussions on the method have been offered, for example, by Chow et al., 1993. For these analyses, all results were reported as mass of an analyte per filter sample and then converted to gram/mile emission factors using appropriate conversions based on sampling conditions.

At the end of each test day, a system blank or TB sample was collected to estimate the dilution tunnel system contribution to the pollutants measured. This assessment of background levels consisted of collection of samples in the same manner as actual emission samples but with some necessary differences. For example, in the TB tests, the bus engine was not running, the bus

exhaust transfer line to the CVS was disconnected, and the CVS bus exhaust inlet was capped. Regulated and unregulated pollutant samples were collected in parallel during this process. All samples were packaged and transported to the laboratory for analysis.

Chemicals

Internal standard solution containing 16 deuterated PAHs was obtained from Cambridge Isotope Laboratories Inc. (Andover, MA). Standard Reference Material SRM 2260 (native PAHs in toluene; nominal 60 ng/μL), was obtained from the National Institute of Standards and Technology (NIST; Gaithersburg, MD). The recovery standards biphenyl-d_{10} and p-terphenyl-d_{14} were obtained from Cambridge Isotope Laboratories Inc. (Andover, MA). Benzo(a)pyrene, 2-nitrofluorene, and dimethylsufoxide (DMSO, HPLC-grade) were obtained from Aldrich Chemical Co. (Milwaukee, WI). Dichloromethane (DCM, OmniSolv) and methanol (OmniSolv) were from EM Science (Gibbstown, NJ). Hexane and acetone were obtained from Burdick and Jackson (Muskegon, MD).

Bioassay Analyses

The bioassay was conducted as previously reported [20] and is a microsuspension procedure that increases the sensitivity over the plate incorporation procedure [21]. The PM extract was re-dissolved in DMSO and added directly to the assay. The PUF extract (in acetone) was solvent exchanged into DMSO under a gentle stream of nitrogen. Tester strains TA98 and TA100 were used with and without the incorporation of microsomal enzymes (±S9). These tester strains are typically used for determining the genotoxicity (DNA damaging) of PM samples from vehicular emissions, ambient air, and environmental samples.

The linear portion of the dose-response curve (line of best fit) was used to calculate the specific mutagenic activity (revertants per mass of PM or per volume of extract for the vapor phase) from each bus configuration and TB test. All sample doses were tested in duplicate and the control values were determined in triplicate. The emissions of mutagenic activity were calculated from the specific mutagenic activity and the total PM or vapor phase emissions per test.

PAH Analyses

Internal deuterated standards were added directly onto the filters before extraction and the filters were extracted with DCM three times by sonication (Bransonic Model 5210R, Branson Ultrasonics Corp; Danbury, CT) for 15 min each time as previously described [6]. Each filter extract was further purified by silica gel chromatography. The hexane/DCM (9:2) fraction was collected for PAH analysis and concentrated to approximately 50 µL. PUF samples were extracted using acetone as previously described [22]. XAD samples were transferred to separatory funnels and extracted four times with DCM. The XAD extracts were filtered and concentrated to 1 mL.

The sample extracts were analyzed for PAHs using a Hewlett-Packard Model 5890 Series II Gas Chromatography interfaced to a HP 5972 Mass Selective Detector. The GC was equipped with a 30 m x 0.25 mm ID DB-5MS fused silica capillary column (0.25 µm film thickness; Agilent Technologies; Palo Alto, CA).

Results and Discussion

Bioassay

Specific mutagenic activity (SMA) refers to the number of revertant bacteria per mass of PM collected (rev/µg PM), tested with or without the addition of metabolic enzymes (± S9), as determined from the linear portion of the dose-response curve for each sample. For all test cycles, a matching and concurrent TB was collected. The specific mutagenic activity SMAs for TA98 are summarized in **Table 3**. The DDC with OxiCat has a lower SMA than the DDC without OxiCat, especially when tested in the CBD cycle. However, overall, the SMAs for the SS cycle are higher than the CBD. When comparing the OxiCats the following is observed. First, for the CBD test cycle, the SMA of the OxiCat-equipped CWest bus was higher than the OxiCat-equipped DDC bus, but lower than the DDC without OxiCat. Second, for the SS cycle, the OxiCat-equipped CWest bus has the lowest SMA of all the bus configurations tested. For all bus configurations, the SMAs for TA98 -S9 were consistently higher than TA98 +S9, which is consistent with other CNG samples that we have previously reported and is indicative of relatively potent compounds in the sample that did not require the addition of metabolic enzymes (direct acting DNA damaging compounds [6]). The TB samples tested concurrently had consistently lower SMAs than the bus samples.

The SMAs for TA100 are also summarized in **Table 3.** For both CBD and SS cycles, the SMAs of the DDC with OxiCat are similar to the DDC without OxiCat (within 15 percent). The TA100 SMAs for the SS cycles are consistently higher than the CBD cycles, except for the CWest OxiCat SMAs. In this case, the SMAs (+S9) are similar to samples tested without metabolic activation (-S9). The CWest OxiCat bus has the lowest SMA for the bus configurations tested for the SS cycle. For all bus configurations, the SMAs for TA100 +S9 were consistently higher than TA100 -S9. In general, this result is consistent for CNG samples previously reported [6] and indicates that compounds that require the addition of metabolic enzymes in this test strain are more potent than compounds that do not require the addition of metabolic enzymes. Results for the CNG-fueled bus TB samples tested concurrently had consistently lower SMAs than the CNG-fueled bus samples. In addition, TA98 and TA100 results for the CNG without OxiCat are consistent with our previous study [6]. To our knowledge, these are the first published results on mutagenic emissions (ME) for CNG-fueled buses equipped with oxidation catalyst.

The SMA of the PM and vapor-phases were used in conjunction with the PM emission rates to calculate the mutagenic emissions (ME) for the samples collected. The MEs from the CBD and SS test cycles for the PM and vapor-phases, as tested in TA98 (±S9), are summarized in **Figure 1** for each bus configuration. For both test cycles, MEs were generally highest for the DDC without OxiCat (1.9-3.8 $x10^5$rev/mi). For example for the CBD cycle (**Figure 1a**), the lowest MEs were observed in the DDC with OxiCat followed by the CWest with OxiCat. However, for the CBD test cycle, the MEs without adding metabolic enzymes were typically higher than the activity with metabolic enzymes, especially for those vehicles with OxiCat. The MEs from buses tested in the SS cycle are illustrated in **Figure 1b**. For the SS cycle, the TA98 (+S9), MEs from the DDC with OxiCat and the CWest with OxiCat were very similar (1.7×10^5 rev/mi and 1.5×10^5 rev/mi, respectively). However, the highest ME was observed for the DDC without OxiCat (**Figure 1b**), and TA98 ME was higher than any of the MEs detected in the CBD test cycle. The vapor-phase MEs were very low relative to the PM-associated MEs for both the DDC with OxiCat and CWest with OxiCat, generally lower than 20% of the total.

The PM and vapor-phase MEs for TA100 (±S9) are summarized in **Figure 2a and 2b** for each bus configuration and test cycle. Overall, MEs were lower with TA100 than those from TA98, which is consistent with CNG samples previously studied [6].

For TA100 (+S9), MEs were generally highest for the DDC without OxiCat over both CBD and SS test cycles (**Figure 2a**). This is consistent with the results observed for tester strain TA98. The TA100 (+S9) PM MEs from buses tested in the SS test cycle are illustrated in **Figure 2b** and it is seen that the DDC with and without OxiCat had similar PM ME values, however the vapor phase ME were higher for the DDC without OxiCat.

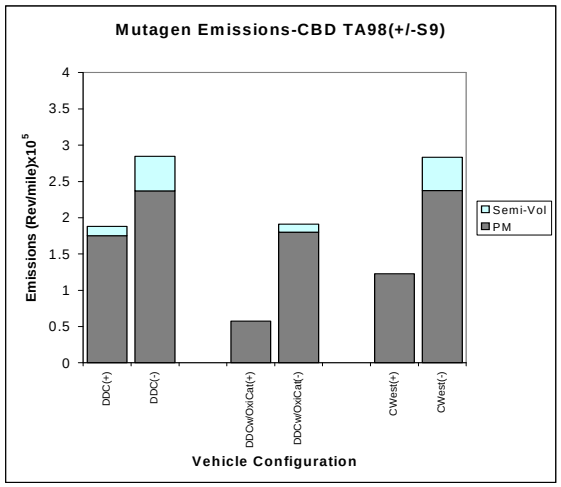
The SMA for the DDC without OxiCat was very similar to the values our group previously reported for the same CNG bus [6]. In previous work, the SMAs for the CBD and SS test cycles were approximately 19 and 40 rev/µg, (TA98, +S9), whereas in the present study they were approximately 16 and 42 rev/µg, respectively. These are remarkably similar values, considering that these emission rates were obtained approximately one year apart and the bus had accumulated approximately an additional 37,000 miles. Another consistent finding is that the ME (-S9) was higher than the ME (+S9) in test strain TA98, possibly due to the presence of compounds that do not require the addition of metabolic enzymes to the test system, such as nitro-PAHs. However, the MEs from buses tested in the current study for both the CBD and SS test cycles were lower than values reported in our previous work, most likely due to the generally lower PM emissions from these buses. The reason for these lower PM emissions is unknown and requires further investigation. From our previously reported work on CNG and diesel with catalyst and diesel equipped with a catalyzed filter trap, we noted that for the CNG fueled bus, the emission levels were approximately 3 times higher than those from the diesel equipped with catalyst, or from the diesel equipped with catalyzed particulate filter [6]. In the current paper, the emissions from the CNG with OxiCat typically range from approximately 25% to 2 times lower than the CNG without OxiCat, depending on the test cycle. We can therefore roughly indicate that relative to CNG without OxiCat, the emission rates for the diesel with catalyst, or the diesel with catalyzed particle filter, decreased the mutagen emissions and were approximately in the same range of decrease. Finally, as described above, the relative MEs from the buses configurations appears to be cycle dependent as described above. The bioassay information is useful to evaluate the relative genotoxic activity of the complex mixture of compounds present in the

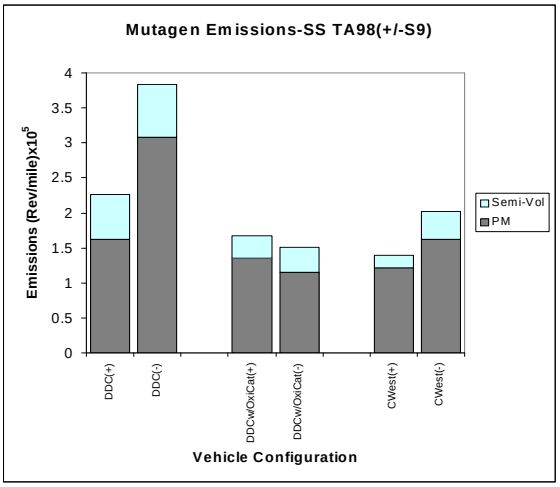
emissions from each engine and control technology. This approach is part of an assessment investigating potential hazard of the emissions.

Table 3. Specific mutagenic activities (SMEs) of PM samples collected during the CBD and SS test cycles. Tunnel background data are presented for comparison. All samples tested in Tester Strain TA98 and TA100with and without metabolic enzymes added (±S9).

	TA98 revertants per µg of PM				TA100 revertants per µg of PM			
	CBD cycle		SS cycle		CBD cycle		SS cycle	
Vehicle configuration	+S9	-S9	+S9	-S9	+S9	-S9	+S9	-S9
DDC w/oOxiCat	16.2	28.1	42.4	61.0	11.2	3.7	38.0	11.5
DDC Tunnel Bkg B	6.0	3.7	6.0	3.7	0.0	0.0	0.0	0.0
DDC wOxiCat	5.8	11.9	37.4	49.9	11.3	4.2	33.0	9.4
DDC Tunnel Bkg A	2.1	2.8	2.1	2.8	0.0	0.0	0.0	0.0
CWest wOxiCat	9.3	17.8	18.0	24.3	7.7	7.6	12.0	6.6
CWest Tunnel Bkg C	0.0	0.0	0.0	0.0	3.3	0.0	3.3	0.0

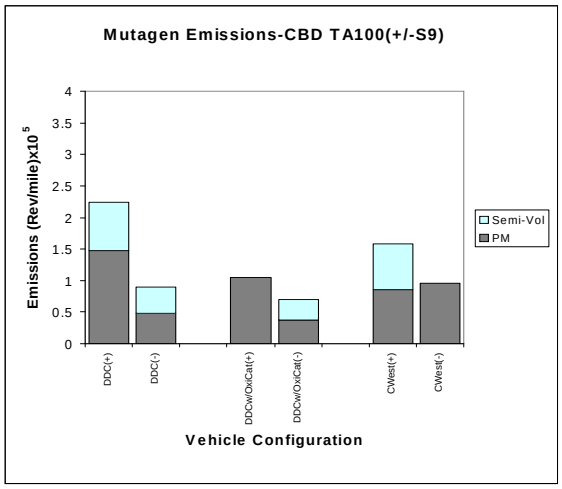
Note: Each value represents six test cycles. The values represent duplicate samples

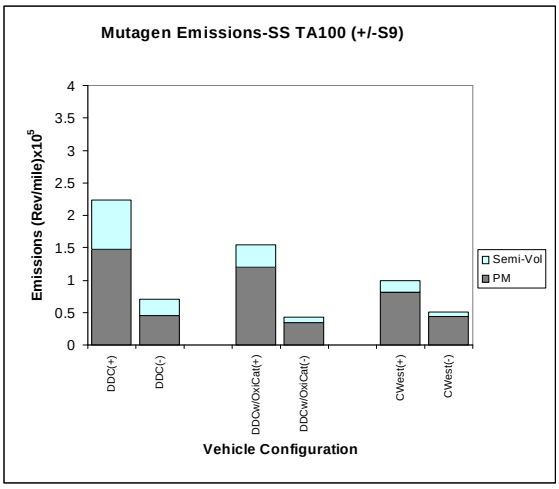




(a) (b)

Figure 1. Mutagenic emissions for each bus configuration and test cycle. Bar represents particle and vapor-phase emissions as tested in TA98 (±S9). (a) CBD test cycle (b) SS test cycle.





(a) (b)

Figure 2. Mutagenic emissions for each bus configuration and test cycle. Bar represents particle and vapor-phase emissions as tested in TA100 (±S9). (a) CBD test cycle (b) SS test cycle.

PAH Analyses

PAH emissions from each bus configuration were determined for the CBD and SS test cycles. Results of PM, semi-volatile and volatile PAH emissions are summarized in Table 4.

Table 4. Emission rates of PM-associated PAHs from CNG Transit Buses configured with and without oxidation catalyst.

PAH	CBD test cycle			SS test cycle		
	DDC w/oOxiCat	DDC wOxiCat	CWest wOxiCat	DDC w/oOxiCat	DDC wOxiCat	CWest wOxiCat
	(µg/mi)					
Naphthalene	77	29	36	49	7.5	6.6
2-Methyl naphthalene	18	7.2	7.3	10	1.9	1.7
1-Methyl naphthalene	9.6	3.8	3.8	5.5	1.0	0.84
Biphenyl	3.4	2.2	1.7	1.5	0.65	0.40
2,6-Dimethyl naphthalene	3.3	2.4	2.1	0.88	0.61	0.54
Acenaphthylene	2.8	.97	.96	1.0	0.28	0.36
Acenaphthene	1.4	1.2	0.75	0.51	0.26	0.057
2,3,5-Trimethyl naphthalene	1.7	1.6	.97	0.70	0.46	0.29
Fluorene	2.1	1.5	1.2	0.91	0.40	0.21
Phenanthrene	7.4	5.2	6.0	4.0	2.0	2.1
Anthracene	0.32	0.17	0.21	0.48	ND	0.10
1-Methyl phenanthrene	1.5	1.9	2.1	0.92	0.89	0.76
Fluoranthene	3.7	3.5	2.3	2.2	1.4	1.7
Pyrene	7.4	5.6	4.3	4.4	2.6	3.2
Total PAH m.w. 128-202	**141**	**67**	**70**	**82**	**20**	**19**
Benz(a)anthracene	0.13	0.11	0.17	0.071	0.042	0.027
Chrysene	0.20	0.13	0.36	0.16	0.094	0.025
Benzo(b)fluoranthene	0.12	ND	0.14	0.035	0.032	0.029
Benzo(k)fluoranthene	ND	ND	ND	0.024	ND	ND
Benzo(e)pyrene	0.074	0.064	0.094	0.028	ND	0.017
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND
Perylene	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	0.13	0.13	ND	0.013	ND	0.031
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	0.12	0.10	0.12	0.031	0.02	0.028
Total PAH m.w. 228-278	**0.77**	**0.53**	**0.87**	**0.37**	**0.18**	**0.16**

ND= less than 0.04 µg /mi for CBD and less than 0.01 µg /mi for SS

Each value represents a composite of six test cycles.

Table 5. CBD and SS PAH Tunnel Background Levels.

PAH	CBD Tunnel Background			SS Tunnel Background		
	DDC w/oOxiCat	DDC wOxiCat	CWest wOxiCat	DDC w/oOxiCat	DDC wOxiCat	CWest wOxiCat
	(µg/mi)					
Naphthalene	73	56	39	17	13	11
2-Methyl naphthalene	11	6.9	7.0	2.6	1.6	1.6
1-Methyl naphthalene	5.1	3.4	3.5	1.3	0.80	0.82
Biphenyl	6	1.4	1.3	0.41	0.32	0.31
2,6-Dimethyl naphthalene	2.6	1.6	2.1	0.63	0.37	0.49
Acenaphthylene	0.67	0.65	0.61	0.16	0.15	0.14
Acenaphthene	0.50	0.47	0.59	0.12	0.11	0.14
2,3,5-Trimethyl naphthalene	0.91	0.93	0.93	0.24	0.22	0.22
Fluorene	0.67	0.75	0.87	0.19	0.17	0.20
Phenanthrene	4.2	3.9	4.4	1.0	0.91	1.0
Anthracene	ND	ND	0.01	ND	ND	ND
1-Methyl phenanthrene	1.6	1.3	1.9	0.43	0.30	0.43
Fluoranthene	1.9	1.8	2.0	0.52	0.43	0.46
Pyrene	2.6	3.1	2.9	0.73	0.72	0.67
Benz(a)anthracene	ND	0.11	0.12	0.03	0.03	0.03
Chrysene	ND	0.08	ND	0.02	0.02	ND
Benzo(b)fluoranthene	ND	ND	0.13	0.03	ND	0.03
Benzo(k)fluoranthene	ND	ND	ND	ND	ND	ND
Benzo(e)pyrene	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND
Perylene	ND	ND	ND	ND	ND	ND
Indeno(1,2,3-cd)pyrene	ND	ND	ND	0.03	ND	ND
Dibenz(a,h)anthracene	ND	ND	ND	ND	ND	ND
Benzo(g,h,i)perylene	ND	ND	0.11	0.02	ND	0.03

Note: ND= less than 0.04 µg /mi for CBD and less than 0.01 µg /mi for SS
Each value represents a tunnel background equivalent in length to three test cycles.

For steady state operation and as expected, the DDC with OxiCat emitted less PM-associated PAHs (m.w. 228-278) than without the OxiCat. In addition, the CWest bus showed similar total PM-associated PAH emissions as the DDC with OxiCat. For the CWest bus operated for the CBD test cycle, chrysene accounted for over 40% of the total PM-associated PAH emissions, which was higher when compared to the other bus configurations. Excluding chrysene, the total PM-associated PAH emissions were similar for all three bus configurations over both test cycles.

Chrysene, benz(a)anthracene, and benzo(g,h,i)perylene were detected in the emission samples from all three bus configurations over both test cycles. Benzo(a)pyrene, perylene, and dibenz(a,h)anthracene were not detected in any of the emission samples. Generally, chrysene dominated the PM-associated PAH emissions for all three bus configurations over both cycles.

When tested under SS conditions, the DDC with OxiCat emitted 41% less chrysene than without the OxiCat.

For the DDC bus with OxiCat for the SS test cycle, the total semi-volatile and volatile PAH emissions were reduced by approximately 76% relative to the DDC bus without OxiCat. Naphthalene was observed to have the highest emission rate of all PAHs measured from all bus configurations tested over both CBD and SS test cycles. This may be noteworthy since the carcinogenic potential of naphthalene is currently under review [23]. For the CBD test cycle, total semi-volatile/volatile PAH (m.w. 128-202) emissions from the DDC with OxiCat were approximately 52% lower than without OxiCat. As illustrated in Table 5, for the SS cruise condition, the DDC without OxiCat had naphthalene emissions of approximately 49 μg/mi, but use of the OxiCat reduced these emissions by 85 % to approximately 7.5 μg/mi. Naphthalene emissions from the CWest bus were similar in magnitude to the emissions from the DDC bus with OxiCat.

In general, the OxiCat on the DDC bus was more efficient at reducing volatile PAHs than PM-associated PAHs. The highest reduction occurred for naphthalene, the most volatile PAH measured, a trend that was more pronounced for the SS test cycle. Presumably, this may be due to sustained high exhaust temperatures over the catalyst during the SS cycle, allowing for improved OxiCat performance. In addition, lower hydrocarbon and NO_X emissions resulting from lower demands on the fuel control system, which limit fluctuations in the air/fuel ratio, may also aid in the catalyst performance. The PAH emissions data suggest that the DDC OxiCat appears to yield higher reductions of volatile, lower molecular weight PAHs than higher molecular weight PM-associated PAHs over the CBD and SS test cycles. However, the data suggests that use of the DDC OxiCat results in greater reductions of PM-associated PAHs during the SS cycle than during the CBD test cycle. The PAH emission profile for the CWest bus with OxiCat was similar to that of the OxiCat-equipped DDC bus. A direct comparison of PAH emission reductions cannot be made on the CWest bus since it was tested only with the OxiCat. However, volatile PAH emissions of the CWest bus appear to be comparable or lower than the DDC OxiCat.

TB samples were collected as previously described. Given in **Table 5** are the TB levels for all bus configurations tested on the CBD and SS test cycles. For the PAHs of m.w. 128-202 except anthracene the coefficient of variation of the three tunnel backgrounds ranged from 1%-30 %. This may be attributed to the extensive tunnel conditioning conducted before the start of each day's test. The TBs for heavier PM bound PAHs has a much greater coefficient of variation ranging from 59%-173%. This may be in part due to the analytical uncertainty, which is higher because of the much lower levels of these PAHs. Also, and perhaps more importantly, the tunnel conditioning procedure may not be as efficient at conditioning PM bound PAHs.

In approximately 50% of the cases, the PAHs measured in the TB samples were less than half the level the level measured from the engine emission samples. Generally, the more volatile the PAHs the higher TB level was in comparison to the level in the emission test sample. However, for the CWest, TB levels for most of the volatile PAH (m.w. 128-166) were at a similar level to PAHs in the emissions over the SS and CBD. For the DDC with OxiCat and DDC without OxiCat about 25% and 15% of the TB, respectively, were at levels at or above 70% of the actual measured emissions. These results may suggest that many of the volatile PAHs emitted from the CWest and to a lesser extent the DDC with OxiCat may be the upper range of their level in the exhaust emissions. To obtain a more accurate measure of these PAHs would require a system with lower TB levels. Also, since TB are not collected under identical conditions as the emission test samples (i.e. no exhaust gas results in different temperature and humidity conditions) therefore, no TB corrections were made to the emissions data. However, the results show that TB are not negligible and the PAHs adsorbed onto the wall of the dilution tunnel have the potential to significantly affect the level of PAHs in the emission samples. This issue is most important for PAHs with high TB levels relative to the sample such as for naphthalene (see previous discussion). Few studies have reported TB levels, but where they have been reported, TB levels may be of concern for PAHs and VOCs from the stand point of the impact on

reporting results [6, 8]. Although extensive conditioning of the tunnel with dilution air was conducted (approximately 105 cubic feet, followed by hot exhaust at steady state for 35 min), for future studies, one approach to fully address the tunnel background effects would be to redesign CVS tunnels. This would include designs that limit deposition and desorption from tunnel surfaces or develop tunnels where deposition of material on the CVS from each emission test can be recovered.

In summary, the emission profile for the CNG-fueled transit buses shows primarily volatile and semi-volatile PAHs (m.w. 128-202) and with heavier PAHs (m.w. 228-278) emitted at very low levels. The low emissions rate of heavier PAHs is similar to newer technology diesel fueled engines equipped with catalyzed particle traps. When compared to our previous results [6], emissions from the DDC without OxiCat were comparable levels of total PAHs in the SS and PM associated PAHs in the CBD. In contrast to the previous study, the DDC without OxiCat showed higher PAH emission rates for volatile and semivolatile PAH for the CBD test cycle. Two other groups also studied emissions from a CNG-fueled transit bus (no OxiCat) equipped with a DDC engine for the CBD test cycle. Of the PAHs measured by the three studies, PAHs with m.w.152-202, our present results were comparable to those reported by Lanni et al [1], but were generally lower than those by Lev-On et al [8]. Again, to our knowledge, this is the first report on the effect CNG OxiCat has on PAH emissions.

PM-associated Inorganic Elements

The emission rates of PM-associated inorganic elements collected on filters for the three bus configurations tested over the two driving cycles are shown in **Tables 6 and 7**. Each emission rate was determined from samples collected over the same time period and at the same nominal flow rate. In this case, again as stated previously, the TB samples (see **Table 8**) are collected in similar fashion to bus emission samples, but the temperature and humidity in the CVS tunnel are different than when the bus is in operation. This is a feature (or shortcoming) inherent to all emission studies. In addition, trip blanks were also analyzed and, although not presented, we can report that the results were negligible.

Inorganic element emission samples were collected in duplicate and analyzed separately, with each sample being the composite result of three individual CBD test cycle equivalents (one test sequence or 30 min of sampling time) as previously discussed. An analytical uncertainty (counting error) for XRF for the detected concentration of each inorganic element was converted to mg/mi as shown in **Tables 6 and 7**. We report results for all analytes that were detected and identify elements according to their expected source. We acknowledge that some elements, which were detected in the filter sample cannot be readily traced back to a related source, hence they are indicated as likely artifact. However, we choose to report all detected elements for completeness and perhaps to underline the challenges associated with collection of such low emissions samples.

As expected, the nominal results suggest that elements are a small fraction of total PM emissions. Previously, we reported total PM emissions on the order of 10 mg/mi to 20 mg/mi for the OxiCat-equipped CNG buses and on the order of 13 mg/mi to 28 mg/mi for the CNG bus without OxiCat [13]. This makes the emissions of inorganic elements at most approximately 5% to 10% of total PM. Transient operation did result in statistically significant higher gram per mile emissions than steady-state operation and in distinct emission profiles as can be seen by comparing **Tables 6** and **7**.

Table 6. Emissions rates of PM-associated inorganic elements for each bus configuration for the CBD cycle.

Element	DDC w/o OxiCat		DDC with OxiCat		Cwest with OxiCat	
	mean	*uncert.*	mean	uncert.	mean	uncert.
Aluminum	0.25	*0.053*	0.18	0.124	0.09	0.121
Calcium**	0.06	*0.016*	0.09	0.016	0.07	0.016
Chromium	0.07	*0.006*	0.05	0.006	ND	
Cobalt	0.11	*0.005*	0.08	0.004	ND	
Copper*	ND		ND		0.01	0.002
Iron*	0.07	*0.006*	0.05	0.005	0.22	0.008
Magnesium**	0.27	*0.354*	0.38	0.154	0.13	0.420
Nickel	0.01	*0.005*	ND		ND	
Phosphorous**	0.01	*0.041*	0.03	0.032	0.01	0.040
Silicon***	0.13	*0.025*	0.12	0.058	0.10	0.059
Sodium***	2.05	*0.608*	0.43	1.772	0.93	1.186
Sulfur**	0.06	*0.014*	0.07	0.013	0.19	0.014
Zinc**	0.04	*0.003*	0.04	0.003	0.03	0.003
TOTAL, mg/mi	3.13	*0.71*	1.52	1.78	1.78	1.27

ND = not detected, less than 0.009, 0.004, 0.005, 0.004 mg/mi for Cr, Co, Cu, and Ni respectively
* = wear metal
** = lubricant additive
*** = likely artifact

Note: Each value represents two replicates (two test sequences) with each replicate consisting of a composite of three test cycles (one test sequence). Uncertainty (uncert as defined in table) is the counting error.

Table 7. Emissions rates of PM-associated inorganic elements for each bus configuration for the SS cycle.

Element	DDC w/o OxiCat		DDC with OxiCat		Cwest with OxiCat	
	mean	uncert.	mean	uncert.	mean	uncert.
Aluminum	0.01	0.04	0.024	0.024	0.01	0.04
Calcium**	0.05	0.004	0.03	0.004	0.01	0.010
Chromium	0.03	0.002	0.02	0.002	0.003	0.001
Cobalt	0.04	0.001	0.04	0.001	0.09	0.001
Copper	0.001	0.001	ND		ND	
Iron*	0.03	0.001	0.01	0.001	0.01	0.001
Magnesium**	0.05	0.071	0.10	0.029	0.11	0.088
Nickel	0.002	0.006	0.002	0.005	ND	
Phosphorous**	ND		ND		0.01	0.005
Silicon***	0.04	0.006	0.02	0.006	0.02	0.006
Sodium***	0.35	0.32	0.35	0.27	0.65	0.15
Sulfur**	0.04	0.004	0.09	0.004	0.73	0.010
Zinc**	0.03	0.001	0.01	0.001	0.02	0.001
TOTAL, mg/mi	0.67	0.33	0.70	0.27	1.68	0.17

ND = not detected, less than 0.001 mg/mi for Copper and Nickel
* = wear metal
** = lubricant additive
*** = likely artifact

Note: Each value represents two replicates (two test sequences) with each replicate consisting of a composite of three test cycles (one test sequence). Uncert. is the counting error

Table 8. Emission rates of PM-associated inorganic elements for each bus configuration and test cycle.

	Mean Emissions (Uncert) mg/mi		
Cycle/Background	**DDC w/o OxiCat**	**DDC wOxiCat**	**CWest wOxiCat**
CBD test cycle	3.16 (0.86)	1.57 (1.84)	1.86 (1.29)
CBD Tunnel Background	0.67 (1.45)	1.08 (1.44)	2.33 (0.61)
SS test cycle	0.71 (0.85)	0.76 (0.72)	1.61 (0.72)
SS Tunnel Background	0.15 (0.33)	0.25 (0.33)	0.53 (0.14)

Note: Each test sample represents two replicates (two test sequences) with each replicate consisting of a composite of three test cycles (one test sequence). Each background is one replicate.

The total emission rates for each corresponding TB are shown in **Table 8**. Cycle results are repeated for convenience. As stated previously, duty cycle effects were discernable statistically. However, nominal TB levels were lower than emission samples, but not statistically significant due to the uncertainty in the results.

The composition of the samples collected over both test cycles for all three buss suggests a dominant presence of Na and Mg, a lubricant additive. For the CWest bus with OxiCat shows Na, Mg, and S were prevalent. Similarly, the composition for the samples from the DDC shows Na and Mg as the most abundant species. It is noted that the relative abundance of S in the CWest sample results and the presence of Na in all samples cannot be readily explained, but may be due to a tunnel history effect from previous testing and to ambient air used for dilution. Finally, for all bus configurations and test cycles, the emissions of toxic elements that were measured such as chromium, copper, and nickel were among the lowest of the species detected.

Elemental and Organic Carbon

Average emission factors for OC and EC as a function of bus configuration and driving cycle are illustrated in **Table 9**. Emissions collected over three CBD cycles (one test sequence) or CBD-equivalent runs (in the case of the SS cruise tests) were summed into one test sequence result. Each test sequence was conducted in duplicate and analyzed separately. Results are presented without correction for tunnel backgrounds. The data for tunnel background samples are also included in **Table 9**. In most instances, average TB "emission" levels were lower than bus emissions. For all bus configurations and over both test cycles, the TB samples were primarily composed of OC. On a gram-per-distance-traveled (gm/mi) basis, carbon emissions were statistically greater for the transient CBD test cycle than for the SS cruise cycle. In addition, over both test cycles and for all bus configurations tested, the total carbon emissions were dominated by OC. The EC to OC ratio, based on average values, ranged from 0.21 to 0.37 over both test cycles. When compared to the DDC bus without OxiCat, OC emissions from the DDC bus with OxiCat were reduced by approximately 27% as measured for the CBD cycle. However, this nominal reduction falls within the standard deviation of the measurement. In addition, for this bus, the average EC emissions were reduced by approximately 12%. In contrast, use of the OxiCat does not appear to result in measurable reductions of carbon emissions for the SS test cycle **(Table 9).**

The two engine technologies exhibited some statistically significant differences in their carbon emissions. For the CBD cycle, the CWest engine, which is OEM-equipped with an OxiCat,

resulted in slightly higher average OC emissions than the DDC bus with OxiCat. It is not entirely clear why the OC emissions from the CWest were higher. However, this trend was also observed for the emissions of total hydrocarbons as previously reported by our group [13]. It is noted that these observations are offered without examination of dilution tunnel history effects that may be present and as suggested by some of the tunnel background results. Furthermore, differences in the age and activity of the catalysts may explain differences in the composition of carbon emissions noted.

Table 9. Emissions of Organic and Elemental Carbon for Each Bus Configuration and Test Cycle.

CBD test cycle	**OC ± Std. Dev. (mg/mi)**	**EC ± Std. Dev. (mg/mi)**	**EC/OC ratio**
DDC w/oOxiCat	10.4 ± 3.0	2.6 ± 2.3	0.25
DDC /OxiCat	7.6 ± 0.0	2.3 ± 0.5	0.30
CWest w/OxiCat	12.8 ± 0.8	2.6 ± 3.1	0.21
SS test cycle			
DDC w/oOxiCat	3.1 ± 0.0	1.1 ± 0.2	0.37
DDC wOxiCat	3.1 ± 0.4	1.1 ± 0.2	0.34
CWest wOxiCat	3.5 ± 0.6	0.7 ± 0.7	0.21

OC = Organic Carbon
EC = Elemental Carbon
Std. Dev. = Standard Deviation
EC/OC = Ratio of elemental carbon to organic carbon

Each sample (CBD, SS, and TB) was collected over the same time period and at the same nominal flow rates. In general, slightly more total carbon mass was collected for the SS test cycle than for the CBD cycle. In all instances, with one exception, average TB levels were lower than bus emissions. The single exception is the TB associated with the sample for DDC bus with OxiCat for the CBD cycle. For all bus configurations and over both test cycles, the TB samples were primarily composed of OC.

Total carbon emissions (sum of the average EC and OC emissions), over both test cycles, were lower than the reported emissions of regulated PM as illustrated in Figure **3**. Total PM emissions have been reported previously by our group, but are included here for convenience [13]. For the CBD cycle, they were approximately 28 mg/mi, 20 mg/mi, and 21 mg/mi for the DDC, DDC with OxiCat, and CWest configurations, respectively. For the SS condition, they were, in the

same order, approximately 13, 11, and 15 mg/mi. Total PM was collected through a secondary dilution tunnel whereas, as previously described, carbon samples were collected from the primary dilution tunnel. The effect of this sampling path difference cannot be ascertained from these results. For the CBD cycle, total PM emissions for the OxiCat-equipped buses were in agreement within 2%, whereas the total carbon emission results were in agreement within approximately 50%. In addition, while PM emission for the DDC without OxiCat bus for the CBD cycle was approximately 25% higher than the PM emissions for the OxiCat-equipped buses, this trend was not observed for total carbon emissions. Similar trends were observed for the SS test cycles in that regulated PM emissions were higher than total carbon emissions, which coincidentally were nominally measured at 4.2 mg/mi for all three bus configurations.

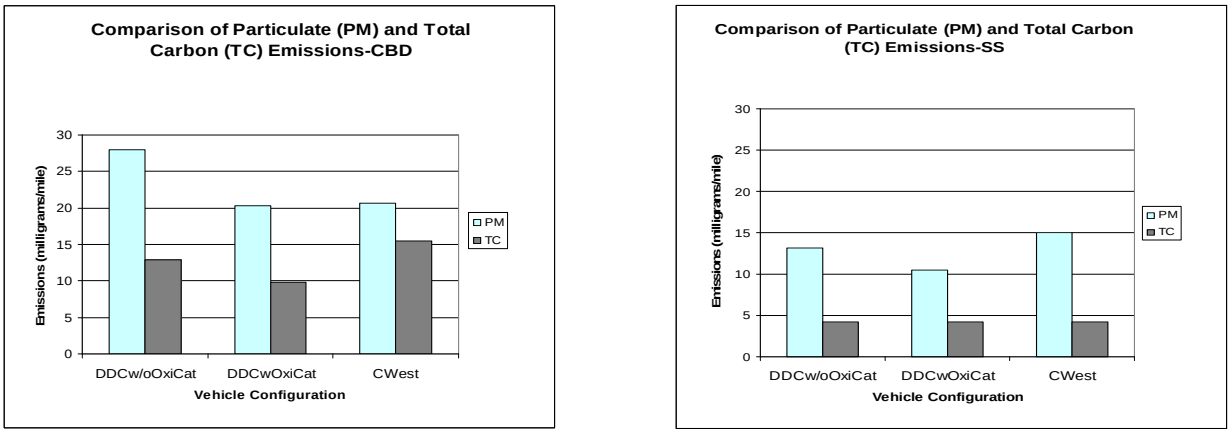


Figure 3. Comparison TC and total PM emissions (mg/mi).

Comparison of Emission Rates

The use of OxiCat for the control of emissions from CNG engines is not a new concept. When a CNG heavy-duty engine is operated without an OxiCat, a major emission is formaldehyde [13, 1, 6]. The use of OxiCat results in average formaldehyde reductions of approximately 95% and 98% for the CBD and SS test cycles, respectively [13]. Other emissions are also reduced as discussed above. Primarily the semi-volatile and volatile PAH emissions are reduced. However, the absolute reduction of PAH emissions by the OxiCat may be cycle dependent. The sustained high temperature for the SS test cycle favors the oxidation of PAHs in the catalyst. In contrast,

the transient nature of the CBD cycle, and hence the variation in exhaust temperature, may result in less efficient reduction of PAHs.

The CNG engine technologies exhibited some statistically significant differences with respect to total carbon emissions. Test cycle effects on carbon emissions were discernable, with CBD emission rate (mg/mi) that were higher than SS emission rate. The composition of PM emissions from CNG buses tested was dominated by OC over both CBD and SS test cycles. The OxiCat-equipped DDC bus resulted in some reduction of average OC emissions. However, the uncertainty in the measurements suggests that these reductions were not statistically significant. Average EC emissions accounted for less than 30% of the OC detected, although greater experimental uncertainty was associated with these measurements. Differences were observed between measured values of total carbon and total PM emissions. PM-associated inorganic elements were observed in emission samples from both CNG buses. However, these emission rates (3.2 mg/mi or less) were greatly exceeded by the emission rates for total PM or total carbon. Unfortunately, the effect of the OxiCat on the emission of inorganic elements was not statistically discernable. The use of the OxiCat in the DDC-powered CNG bus resulted in decreased mutagenic activity of the emissions from this bus in tester strain TA98 with and without S9 activation.

Finally, to gain further insight into the emissions profile from the three CNG bus configurations tested, the relative emissions of key species were compared for both the SS and CBD test cycles, as shown in **Figures 5 and 6,** respectively. For simplicity, all emission rates were normalized to the PM emissions from the DDC bus without OxiCat and were scaled to fit into one figure. The SS cycle results show somewhat similar emission profiles for the OxiCat-equipped configurations (DDC and CWest). In contrast to the SS, relative emission rates of total TA 98 +S9 mutagenicity, and PAHs of molecular weight 228 and greater for the CBD were higher for the CWest bus with OxiCat than for the DDC with OxiCat. This suggests higher activity for the newer DDC OxiCat than the CWest OxiCat which allows for the more efficient reduction over a driving cycle less conducive to OxiCat operation such as the CBD that consists of varying and at times mild exhaust temperatures.

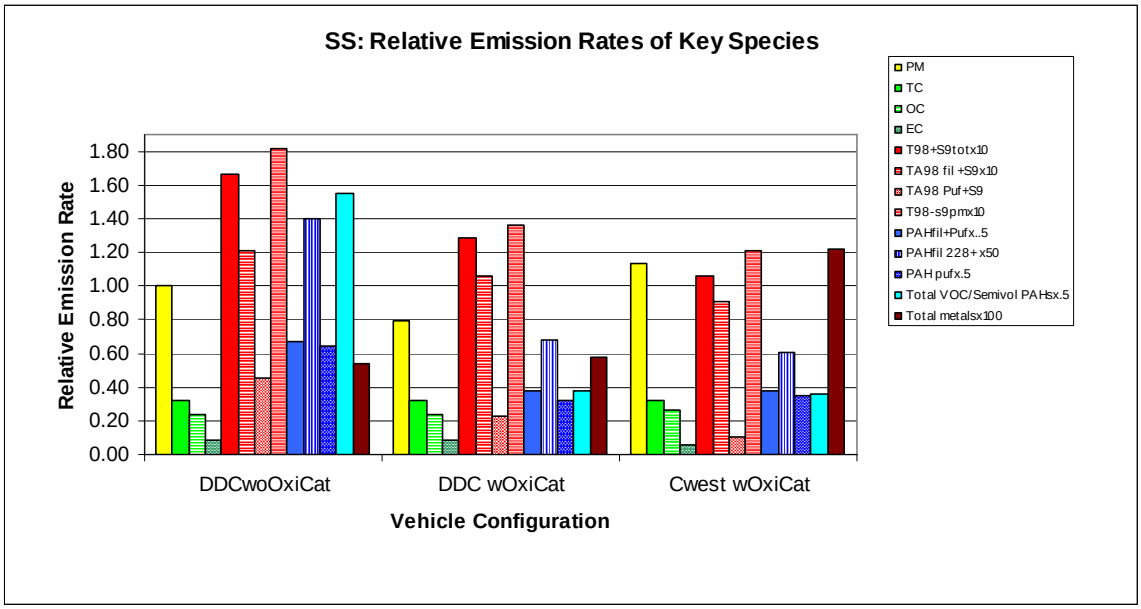


Figure 5. Relative emission rates of key species normalized to DDC PM emissions for each bus configuration tested in the steady state mode. Some of the species are multiplied by a factor to fit on the same figure.

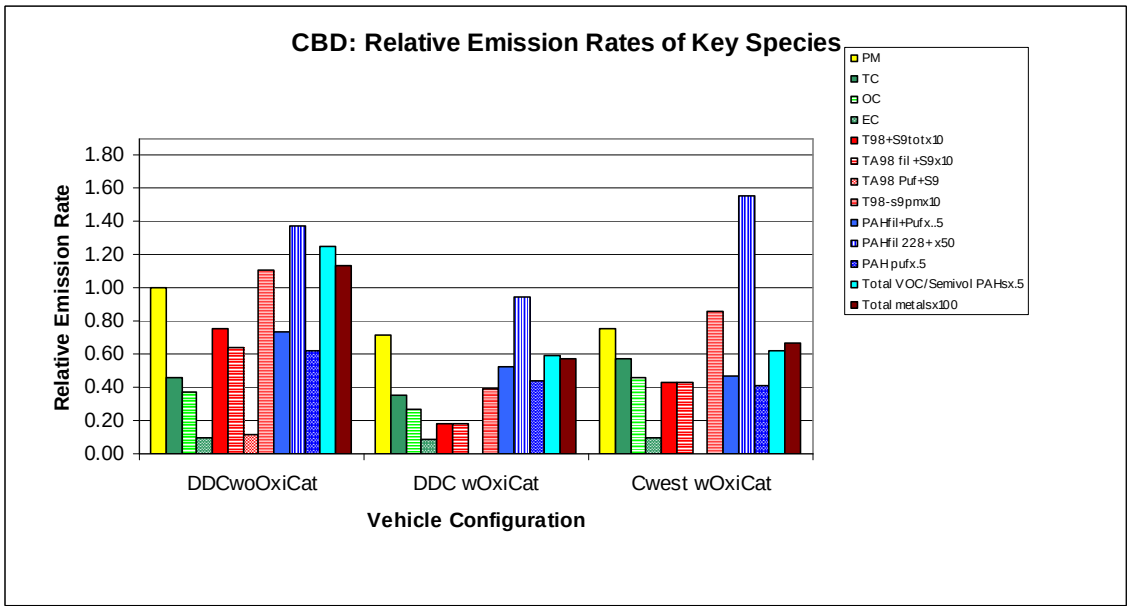


Figure 6. Relative emission rates of key species normalized to DDC PM emissions for three bus configuration tested in the CBD cycle. Some of the species are multiplied by a factor to fit on the same figure.

Durability or deterioration of the OxiCats and lubricating oil consumption were not addressed in this study. It has been reported that precise control of the air/fuel ratio is critical for the

performance of the emission control system and that as the catalyst ages the ability to achieve optimum air/fuel ratio decreases [11]. Thus, a decrease in durability may be a greater problem in retrofit, older-technology engines with open-loop fuel systems and less advanced control of air/fuel ratios. In addition, odorants used in the CNG fuel at concentrations as low as 10 to 15 mg/m^3 of gas can have a detrimental effect on the conversion efficiency of Pd/Alumina-based OxiCats in lean burn natural gas engines [11]. To our knowledge, the effect of catalyst aging on PM, PAH, nitro-PAH, and mutagenic emissions is not known. Although the data obtained from this study is limited in scope, the emissions from the test buses most likely typify the expected difference between the technology options investigated, these results cannot be used to infer fleet-wide conclusions, thus future research is needed to address these areas.

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